PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SHIMADZU CORP
(72)Inventor : YAMAMOTO YOSHITAKE

(54) DATA PROCESSING DEVICE FOR MASS SPECTROMETER/MASS SPECTROSCOPE

(57)Abstract:
PURPOSE: To facilitate fixing of a parent ion by determining the candidates thereof by making reference to the database of structure establishing rules storing rules for establishing the parent ion from each type of daughter ion and detached group.
CONSTITUTION: A peak analysis section extracts peak ion candidates and detached group candidates regarding all peaks, and the data of the extraction is sent to a parent ion estimation section. In addition, a parent ion estimation section first prepares the combinations of daughter ions and detached groups likely to become mass, on the basis of the data of mass spectra, and ion and leaving group candidates. Thereafter, the estimation section calculates the possibility of the combinations, referring to rules in the database of structure establishing rules, regarding each of possible combinations. Also, the estimation section estimates the structure of parent ions according to the order of high probability by referring to the peak height of mass spectra. Finally, parent ion candidates resulting from the estimation are shown on a display in the order of high probability.

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[Claim(s)]

[Claim 1] The data processor for MS/MS mass spectroscopes which extracts the mass spectrum of the daughter ion which clove the parent ion in the cleavage section by choosing a parent ion in the 1st mass-filter section, and was generated by cleavage characterized by providing the following in the 2nd mass-filter section. a) The peak database which stored the information on the ion kind corresponding to each of various mass. b) The leaving-group database which stored the mass of a leaving group and the information on a leaving-group kind from which it may be desorbed by cleavage. c) A peak-detection means to calculate the desorption mass which detected the peak from the mass spectrum by which extraction was carried out [above-mentioned], and subtracted the peak mass from peak mass and the mass of a parent ion about each peak. d) While extracting the candidate of the ion kind corresponding to the peak mass by referring to a peak database about each peak A peak analysis means to extract the candidate of the leaving group corresponding to the desorption mass by referring to a leaving-group database, e) by referring to the structure construction rule database which stored the rule at the time of building a parent ion from various daughter ions and a leaving group, and f structure construction rule database A parent-ion presumption means to determine the candidate of a parent ion based on the analysis result by the mass of a parent ion, and the peak analysis means, and the height of each peak.

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the data processor which analyzes the data obtained by the MS/MS mass spectroscope. In addition, mainly, in fields, such as a chemical and food, a MS/MS mass spectroscope uses together with a liquid and a gas chromatograph for trace analysis, or is independent, and is used.

[0002]

[Description of the Prior Art] Although it is only detecting the total mass of ion in the usual mass spectroscope, the information about the structure of a parent ion can be acquired in a MS/MS mass spectroscope by detecting the spectrum of the daughter ion which clove and generated the ion (parent ion) by cleavage. Thereby, identification of a parent ion (sample)

becomes easier.

[0003] A MS/MS mass spectroscope chooses and detects the daughter ion which clove and generated the parent ion which was equipped with three steps of quadrupoles arranged in series, chose the parent ion in the quadrupole of the 1st step, and was chosen in the quadrupole of the 2nd step by cleavage in the quadrupole of the 3rd step. Therefore, the data obtained from a MS/MS mass spectroscope serve as the mass mp of a parent ion, and a mass spectrum pattern of a daughter ion.

[0004]

[Problem(s) to be Solved by the Invention] In the usual mass spectroscope, the information on a compound (a compound name, structure), the mass number of a fragment ion, and the strong checklist are beforehand prepared as the library of data about many compounds, and a compound can be identified by collating the mass number of each peak of a spectrum with it. On the other hand, although cleavage gas is introduced into a quadrupole and a parent ion is cloven by the collision with cleavage gas in the 2nd step of a MS/MS mass spectroscope, a parent ion cleaves in various modes by the difference in the collision energy at this time. For this reason, it is difficult for the pattern (the appearance position and height of a peak) of the mass spectrum of the daughter ion obtained to become very various, and to make all patterns into such a library beforehand. For this reason, conventionally, the library pattern was narrowed down to some extent based on the information (for example, amino acid sequence etc.) about the structure of the parent ion (sample) obtained separately, and the method of taking matching in it was used. since [however,] this is work which requires experience when a certain information over a parent ion is needed separately -- anyone -- although -- it was not able to say [identifying a parent ion simply and] Moreover, since library data did not exist about all patterns, when it was not able to identify, it was.

[0005] The place which accomplishes this invention in order to solve such a technical problem, and is made into the purpose is to offer the data processor for MS/MS mass spectroscopes which made identification of a parent ion easy.

[0006]

[Means for Solving the Problem] The data processor for MS/MS mass spectroscopes concerning this invention accomplished in order to solve the above-mentioned technical problem Choose a parent ion in the 1st mass-filter section, and the parent ion is cloven in the cleavage section. The peak database which is the data processor for MS/MS mass spectroscopes which extracts the mass spectrum of the daughter ion generated by cleavage in the 2nd mass-filter section, and stored the information on the ion kind corresponding to each of a various mass, b) The leaving-group database which stored the mass of a leaving group and the information on a leaving-group kind from which it may be desorbed by cleavage, c) A peak-detection means to calculate the desorption mass which detected the peak from the mass spectrum by which extraction was carried out [above-mentioned], and subtracted the

peak mass from peak mass and the mass of a parent ion about each peak, d) While extracting the candidate of the ion kind corresponding to the peak mass by referring to a peak database about each peak A peak analysis means to extract the candidate of the leaving group corresponding to the desorption mass by referring to a leaving-group database, e) by referring to the structure construction rule database which stored the rule at the time of building a parent ion from various daughter ions and a leaving group, and f structure construction rule database It is characterized by having a parent-ion presumption means to determine the candidate of a parent ion based on the analysis result by the mass of a parent ion, and the peak analysis means, and the height of each peak.

[0007] In addition, the parent ion itself which did not cleave in the cleavage section may be contained in the daughter ion which constitutes the spectrum extracted in the 2nd mass-filter section.

[0008]

[Function] A peak-detection means detects a peak by predetermined criteria from the mass spectrum extracted in the 2nd mass-filter section, and calculates the desorption mass mr (=mp-md) which subtracted the peak mass md from the peak mass md and the mass mp of a parent ion about each detected peak. A peak analysis means extracts the candidate of the ion (daughter ion) corresponding to the peak by collating the peak mass md with a peak database first. The number of candidates may be one and they may become [two or more]. similarly, the candidate (one or more) of the leaving group corresponding to the peak is extracted by collating the desorption mass mr with a leaving-group database A peak analysis means performs such processing about all the detected peaks, and extracts a daughter-ion candidate and a leaving-group candidate. A parent-ion presumption means determines the candidate of a parent ion by referring to a structure construction rule database based on the mass of a parent ion, these daughter-ion candidates, a leaving-group candidate, and the height of each peak. The combination which sees from the mass of a parent ion and cannot live together mutually is among many daughter-ion candidates and leaving-group candidates, and the combination of the basis from which it is easy to secede by high probability conversely, and a daughter ion exists. These information is stored in the structure construction rule database, and a parent-ion presumption means determines the candidate of a parent ion as the high order of probability.

[0009]

[Example] Drawing 1 explains the structure of a MS/MS mass spectroscope and operation using the data processor which is one example of this invention. The sample separated by the liquid chromatograph, the gas chromatograph, etc. or the sample introduced directly is ionized in an ionization chamber 11. Each ionizing method used from the former, such as APCI (AtomosPheric Chemical Ionization= atmospheric pressure chemical ionization method), and CI (Chemical Ionization= chemical ionization method), TSP (the ThermoSpray

Ionization= heat spray ionizing method), can be used for ionization. The ionized sample is pulled out by the extraction electrode and introduced into the 1st step quadrupole 13 with the ion lens 12. The superposition voltage of a direct current and a RF is impressed to the 1st step quadrupole 13 from the 1st RF/DC voltage impression section 23, and only the ion (parent ion) which has the predetermined mass number (m/z) mp passes the 1st step quadrupole 13, and goes into the 2nd step quadrupole 15. In addition, in order that the 1st RF/DC voltage impression section 23 may operate with the control signal from the 1st QP control section 41 (drawing 2) in a control section 30, the mass mp of the parent ion which passes the 1st step quadrupole 13 serves as known in the control section 30.

[0010] The 2nd step quadrupole 15 is contained in the container 14 (cleavage room), and cleavage gas is introduced in this cleavage room 14. The parent ion which passed the 1st step quadrupole 13 collides with cleavage gas in this cleavage room 14, and is divided into a daughter ion and a leaving group. although various modes of this cleavage come out, there are and being cloven in a portion with the general weakest combination, depending on collision energy, cleavage is produced also in the portion of a comparatively strong combination Therefore, although the daughter ion of various mass is generated in the cleavage room 14, these daughter ions are introduced into the 3rd step quadrupole 16 by the 2nd step quadrupole 15. In addition, the driver voltage of the 2nd step quadrupole 25 is impressed from the 2nd RF/DC voltage impression section 25.

[0011] In the 3rd step quadrupole 16, only the daughter ion of mass md according to the RF/DC superposition voltage impressed by the 3rd RF/DC voltage impression section 26 is passed like the 1st step quadrupole 13. The daughter ion which passed the 3rd step quadrupole 16 is detected by the detector 17, and a detecting signal is transmitted to a control section 30 through A/D converter 27. The 3rd QP control section 42 (drawing 2) in a control section 30 scans the mass md of the daughter ion which passes the 3rd step quadrupole 16 by changing the control signal given to the 3rd RF/DC voltage impression section 26 one by one. Thereby, in a control section 30, the mass spectrum of the daughter ion produced by cleavage is acquired.

[0012] A control section 30 is the computer equipped with CPU, ROM, and RAM, and external storage 31 and the display 32 grade are connected there. The control section 30 is functionally constituted by the peak-detection section 43 besides the above 1st and the 3rd QP control sections 41 and 42, the peak analysis section 44, and the parent-ion presumption section 45 grade. Moreover, in external storage 31, it has the peak database 46, the leaving-group database 47, and the structure construction rule database 48. The peak database 46 stores the ion kind which has various mass and the mass of those as a contrast table, and the leaving-group database 47 stores the leaving group (usually neutral) which has various mass and the mass of those as a contrast table. Moreover, a structure construction rule database stores the various rules at the time of building a parent ion from various parts (a daughter ion,

leaving group, etc.), such as a possible combination of various ion and a leaving group, and its joint (or separation) energy.

[0013] The flow chart of drawing 3 explains the procedure of data processing which a control section 30 performs. first, the peak-detection section 43 -- the [the detecting signal from a detector 17, and] -- a mass spectrum is created based on the scanning signal (daughter-ion mass md) from the 3QP control section 42, and predetermined criteria detect all the peaks in it (Step S1) As criteria of the peak detection at this time, the point that the inclination of a spectrum curve became beyond a predetermined value, for example is made into the start point of a peak, and after an inclination serves as zero and is subtracted after that, methods, such as making into the point ending [peak] the point that the absolute value turned into below the predetermined value, can be taken. An end of all peak detections detects [next] the mass md about each detected peak (Step S2). Moreover, the peak mass md is subtracted from the mass mp of the parent ion obtained from the control signal of the 3rd QP control section 42, and the desorption mass mr (=mp-md) is computed (Step S3).

[0014] These data are passed to the peak analysis section 44 after the peak-detection section 43 detects md and mr about all peaks by the above-mentioned processing (step S4). In the peak analysis section 44, all the ion (peak ion candidate) that has the mass md is extracted by collating the daughter-ion mass md of each peak with the data of the peak database 46 (Step S5). Moreover, all the leaving groups (leaving-group candidate) that have the mass mr are extracted by collating the desorption mass mr with the data of the leaving-group database 47 (Step S6). In addition, in these steps, it is desirable to give predetermined width of face to the ion mass and desorption mass which were detected, and to search a database within the limits of the width of face.

[0015] In this way, after the peak analysis section 44 extracts a peak ion candidate and a leaving-group candidate about all peaks, those data are sent to the parent-ion presumption section 45. The parent-ion presumption section 45 creates first the combination of a daughter ion and a leaving group which may serve as mass mp based on the data of the data of a mass spectrum, an ion candidate, and a leaving-group candidate. Here, the daughter ion and leaving group which constitute combination may be three or more pieces. Next, the possibility of such a combination is computed by referring to the rule in a structure construction rule database to each of a possible combination. And the structure of a parent ion is presumed in the high order of probability by collating with the peak height of a mass spectrum (Step S7). At the end, the candidate of the parent ion which is the result of presuming is displayed on a display 32 at the high order of probability (Step S8).

[0016] In addition, the severity of the permission width of face in the case of peak top mass md detection of a mass spectrum and the degree of application of a structure construction rule is ranked beforehand, and analyst can also enable it to choose a rank beforehand as an option. When this chooses a loose rank, many parent-ion candidates can come to be outputted, and

analyst can choose now a thing suitable based on other information (information about a sample extraction part etc.). On the other hand, when a severe rank is chosen, one parent-ion candidate comes to be outputted, and he can determine a parent ion, without a beginner also straying. Even in this case, although the probability which is the parent ion is the maximum, a display to that effect is given to a low case, and it is made to output to it as an absolute value of probability, of course.

[0017]

[Effect of the Invention] In the data processor for MS/MS mass spectroscopes concerning this invention, it does not only judge by the whole spectrum pattern of a daughter ion like before, but the information about corresponding ion and a corresponding leaving group is extracted from a database for every peak, and a parent ion is identified based on the probability of the combination. for this reason -- even if there is no corresponding spectrum pattern in a database, identification of a parent ion is attained, and there is no information about a parent ion beforehand -- ** -- identification becomes possible For this reason, identification of a sample is attained even if it is not an expert like before.

[Brief Description of the Drawings]

[Drawing 1] The outline block diagram of the MS/MS mass spectroscope with a data processor which is one example of this invention.

[Drawing 2] The block diagram showing the functional composition of a control section.

[Drawing 3] The flow chart which shows the procedure of data processing which a control section performs.

[Description of Notations]

11 -- Ionization chamber 12 -- Ion lens

13 -- The 1st step quadrupole 14 -- Cleavage room

15 -- The 2nd step quadrupole 16 -- The 3rd step quadrupole

17 -- Detector

23, 25, 26 -- RF/DC voltage impression section

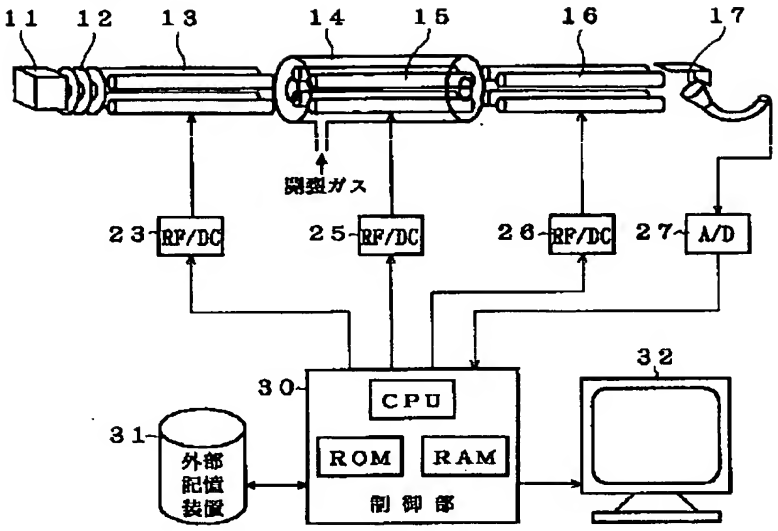
27 -- A/D converter

30 -- Control section

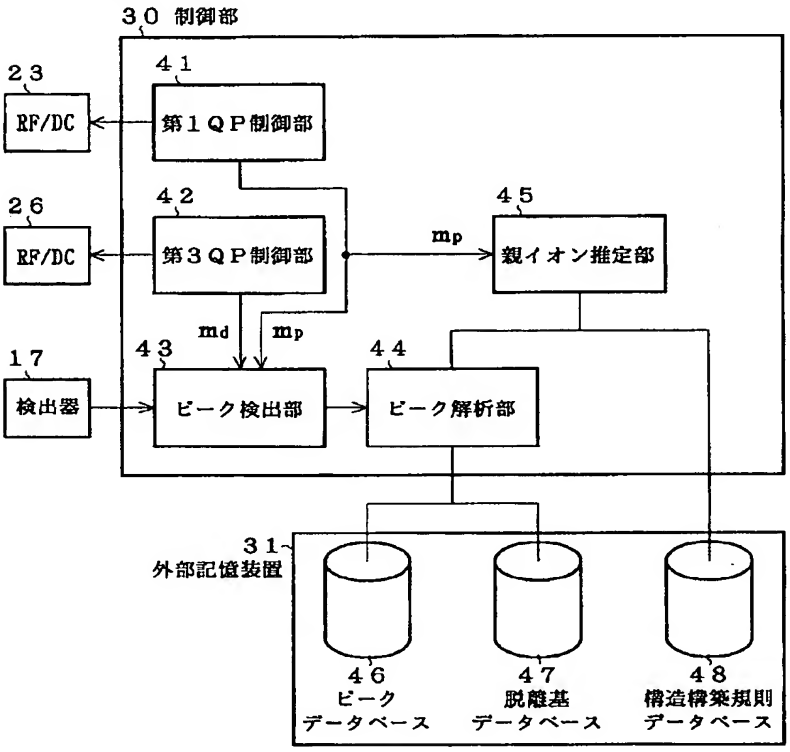
31 -- External storage

32 -- Display

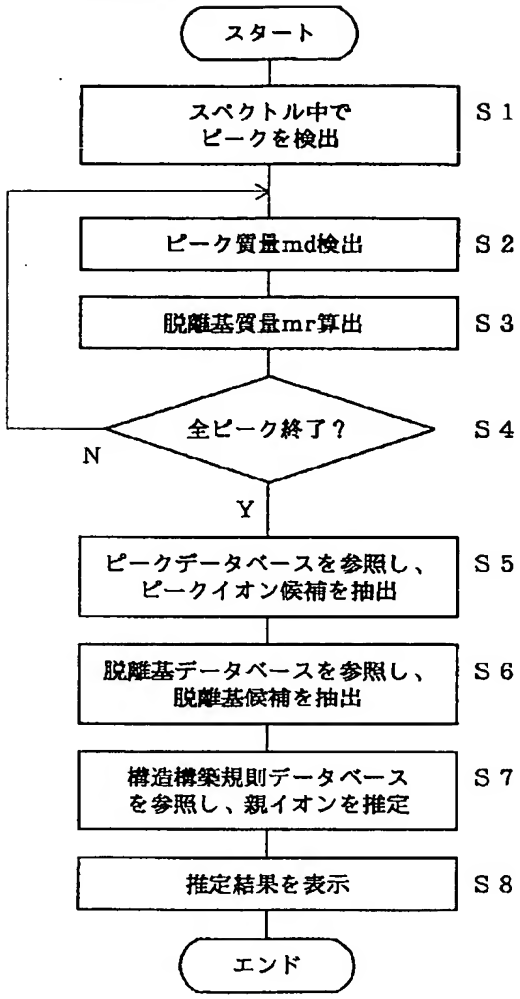
[Drawing 1]



[Drawing 2]



[Drawing 3]


スタート
スペクトル中で
ピークを検出
S 1
ピーク質量md検出
S 2
脱離基質量mr算出
S 3
全ピーク終了？
S 4
N
Y
ピークデータベースを参照し、
ピークイオン候補を抽出
S 5
脱離基データベースを参照し、
脱離基候補を抽出
S 6
構造構築規則データベース
を参照し、親イオンを推定
S 7
推定結果を表示
S 8
エンド